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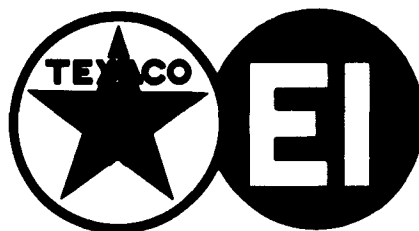
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RICHMOND 2, VIRGINIA

INVESTIGATION OF THE DISSOCIATION
CHEMISTRY OF -NF_2 COMPOUNDS

Quarterly Summary Report for
November 1962 through January 1963

TM-1407

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CONTENTS

	<u>Page</u>
SUMMARY	3
INTRODUCTION	3
THERMAL DISSOCIATION EXPERIMENTS	4
FLASH PHOTOLYSIS	6
FUTURE WORK	11
REFERENCES	11

SUMMARY

The testing and debugging of equipment for both the photolytic and thermal dissociation studies of -NF_2 compounds has now been completed. The design of the flash tubes used in the photolysis work has been modified to minimize the occurrence and inconvenience of exploding tubes, flash durations have been timed, and the sequential flash-delay circuit has been calibrated. Preliminary spectral studies have been started. The adiabatic compression apparatus has been tested on the mass spectrometer with inert gases and was found to operate satisfactorily. The high-speed drum camera has been received and coupled with the apparatus. Breakdown of the mass spectrometer and difficulty in obtaining satisfactory photographic registration of the successive oscilloscope traces of the mass spectrometer output have prevented the start of actual experimentation during this quarter, but these difficulties have now been overcome.

INTRODUCTION

The high-energy propellant possibilities associated with the NF_2 group have led to the development of an extensive new field of chemistry. The synthetic possibilities of now-available reagents such as N_2F_4 , NF_3 , HNF_2 , N_2F_2 , etc. are suggested by the host of new compounds already prepared. It appears, however, that these and similar compounds could be more effectively exploited, both as high-energy oxidizers and as synthesis reagents, if more were known about their dissociation chemistry. It is known, for example, that N_2F_4 is in equilibrium with NF_2 radicals, and appreciable concentrations of NF_2 can be formed with only moderate heating (1). Mechanisms have been proposed for the subsequent participation of the NF_2 radical in reactions; however, the rate of dissociation of N_2F_4 is not known at various temperatures, nor is the rate of dissociation of the NF_2 radical known. One can conceive of situations where the desired chemistry is frustrated because thermal dissociation reactions take place more rapidly than displacement or addition reactions, and vice versa. Because of the potential importance of this class of compounds, it seems important to conduct research designed to give fundamental knowledge of the dissociation chemistry of the -NF_2 compounds.

THERMAL DISSOCIATION EXPERIMENTS

The rationale of the thermal dissociation experiments and a description of the adiabatic compression apparatus to be used in carrying them out have been described in a previous report (1). Briefly, a mixture of approximately 1% NF_3 (for example) and 1% argon in helium is leaked into the adiabatic compression cylinder at a pressure of about 1 to 2 torr. The cylinder is attached to the Bendix time-of-flight mass spectrometer through the fast-reaction cell, and as the compression is carried out, gas from the cylinder is leaked continuously into the ion source chamber of the spectrometer. Mass spectra of the gas are obtained at 50- or 100- μsec intervals by photographing the sequence of oscilloscope traces with a drum camera. From these sequential spectra, the kinetics of the dissociation may be obtained and the species involved identified.

At the time of the last report (1) the adiabatic compressor had been completed but had not been tested nor the piston-travel time measured. The compressor was subsequently tested, both on and off the mass spectrometer, and was found to operate satisfactorily. It was found that a 0.0005-inch-diameter pin-hole (in 1-mil gold foil) gave a satisfactory leak rate into the spectrometer with an initial pressure of 1 torr. The time for the maximum 6.5-inch compression stroke has been measured to be 10 msec. As can be seen from Figure 1, which is a plot of stroke length versus temperature and pressure for adiabatic compression, the last 50° of temperature rise will occur in a time much less than a millisecond. This is especially apparent at the higher final temperatures where the temperature increase is very rapid and the piston has accelerated to very high velocities. We are confident that the heating will be essentially adiabatic. Our complication might be the inevitable bounce of the piston at the end of the stroke, resulting in a slight cooling down from the maximum temperature. It has been found that a felt washer gives optimum deceleration of the piston with minimum bounce. There is still a slight amount of bounce remaining, but it can be measured and partially compensated for. There are some possible techniques for further reduction of the bounce, but it seems inevitable that there will be a slight uncertainty in the final effective temperature.

The mass spectra are to be presented on an oscilloscope and photographed with a Beckman and Whitley Model 364 drum camera, which has been purchased for this purpose. Since the information contained in each sweep of the oscilloscope beam must be clearly recorded without being obscured by the previous trace or smeared on the moving film, a low persistence P-16 phosphor was used.

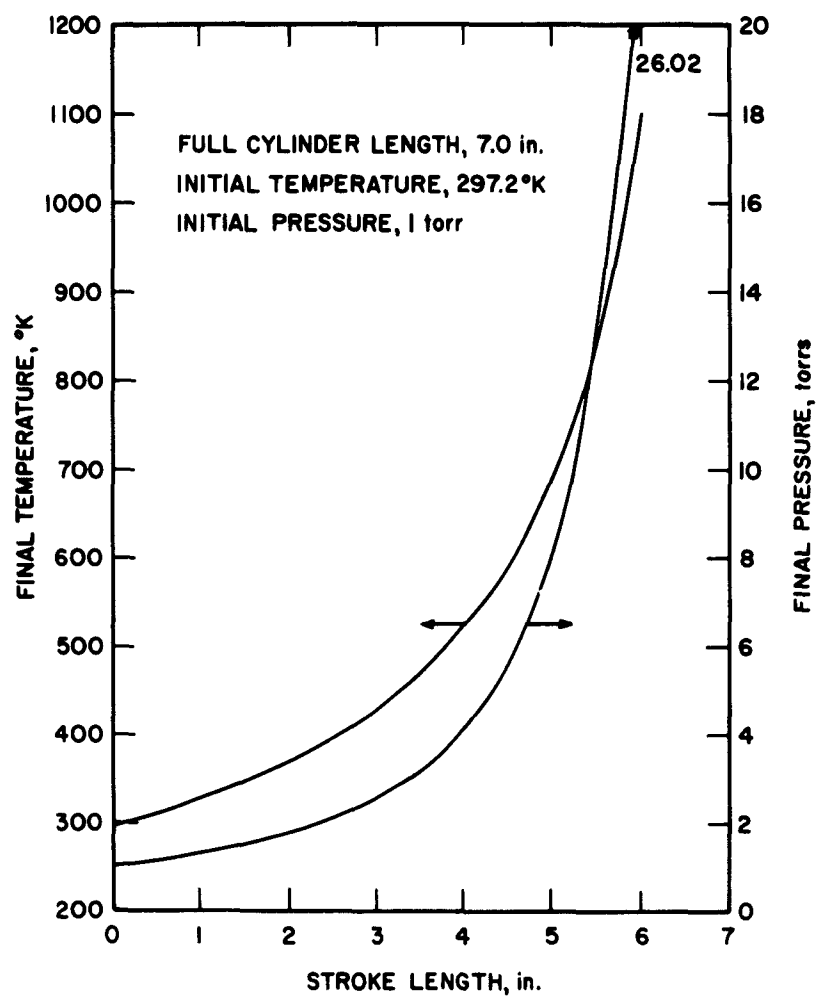


FIGURE 1. FINAL TEMPERATURE AND PRESSURE VERSUS STROKE LENGTH IN ADIABATIC COMPRESSION

Unfortunately, the P-16 spectral output peaks at 3800 Å, which is considerably below the maximum sensitivity of readily available fast films. (Agfa Isopan Record, for example, has a speed of 1250 at 4250 Å but virtually no speed at 3800 Å. Kodax Tri-X and Kodak uv spectrographic film were also unsatisfactory.) We were, however, able to obtain a sample of Kodak SO-234, which has maximum sensitivity at 3800 Å, and has proved to be more than adequate for our purposes and has enabled us to obtain high-contrast photographs of the oscilloscope trace. With the camera running at maximum speed and the mass spectrometer operating at 10 kc, a series of about 70 sequential mass spectra are obtained.

It has also been necessary to build a sequential triggering circuit for the apparatus. Since the camera is run with the shutter open, this device is required to prevent the oscilloscope from being on longer than one revolution of the camera and to insure that the oscilloscope comes on at the right moment. The proper sequence would be for the moving piston to trigger the oscilloscope so that spectra would start being recorded approximately 1 msec before the completion of the compression stroke and then by means of a delay circuit to blank the oscilloscope after about 7 msec. A block diagram of this apparatus is shown in Figure 2.

FLASH PHOTOLYSIS

The flash-photolysis and kinetic-spectroscopy studies of the dissociation chemistry of -NF_2 compounds are now proceeding at a good rate. The motivations for applying this technique to NF_2 studies were briefly reviewed in the last quarterly report (1). A general discussion of kinetic spectroscopy has recently been given by R. G. W. Norrish (2).

Circuit diagrams for the electronic components and a general description of the apparatus were presented in the last quarterly report (1). All of the electronic equipment associated with the apparatus is now in good order. Several minor changes have been made, including the introduction of additional safety devices. It was found that the Tesla coil initially used to trigger the photolysis flash was radiating sufficient energy to trigger the source flash at the same time, so that there was no delay between the two. The Tesla coil has therefore been replaced with a "noise-free" triggering device.

Since there are occasional explosions of the photolysis flash tubes, their design has been changed to facilitate replacement. Instead of sealing off the tubes, they are left connected to a gas manifold through a modified electrode

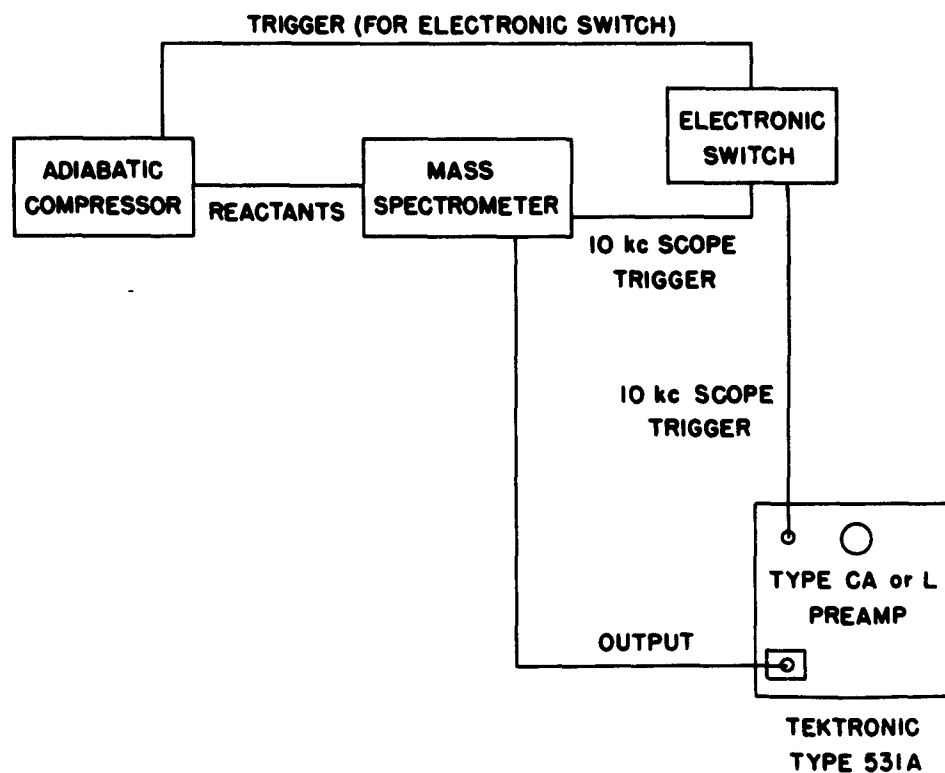


FIGURE 2. BLOCK DIAGRAM OF THE ADIABATIC-COMPRESSOR AND MASS-SPECTROMETER SETUP

sealed to the ends of the quartz envelope by Swagelok fittings and O-rings. These explosions are the unavoidable consequence of the shock wave produced by the discharge of more than 1000 joules in about 30 μ sec. Heavy-wall quartz tubing has been ordered which will help to eliminate this problem. It is not a serious problem; while some tubes have lasted only for a dozen flashes, others have survived more than 50 flashes. Naturally, when the highest voltages are used ($\sim 10,000$ volts), there is a greater chance of rupture. The present arrangement also helps by providing a buffer volume for the pressure wave accompanying the discharge and allows the gas pressure in the tube to be monitored. Argon was found to be a satisfactory gas for the flash tubes and is now used rather than xenon.

Following the debugging of the electronic equipment and the modification of the flash tubes, the photolysis and source flash durations were timed and the delay system calibrated. The flash durations were measured by a cathode follower circuit with an ultraviolet-sensitive phototube and an oscilloscope. Typical oscillograph traces are shown in Figures 3 and 4. Delay times between the two flashes were measured by the same device. The delay can be varied from several to 300 μ sec. A typical delay measurement is shown in Figure 5.

Upon the completion of the timing measurements and delay-circuit calibration, attention was shifted to the spectroscopy of the problem. It was found that a single source flash (100 joules) produced sufficient blackening of the plate to be useful for absorption studies over most of the accessible spectrum. A spectrum of the light from the source flash is shown in Figure 6 along with the iron-arc calibration. It will be noticed that it is essentially all continuum with relatively few emission lines and absorptions. Some difficulty was encountered in eliminating radiation from the photolysis flash reflected into the slit of the spectrograph, but this problem has been solved.

Since NF_3 does not absorb in the visible or the quartz ultraviolet portion of the spectrum ($\lambda > 2000 \text{ \AA}$), nitric oxide is being used as a sensitizer. It is not required that the sensitizer be completely unreactive with the sensitized molecule, but only that the rate of the reaction be slow compared with the reaction under investigation. There is good reason to believe that this is the case with NO and NF_3 . Nitric oxide has the desirable feature of being easily excited to high populations of excited states without dissociating (3). Experiments are now under way in which the spectrum of flashed NO is being studied as a preliminary to studying mixtures of NO with NF_3 . Similar experiments with N_2F_4 will follow, including some without sensitizers, and will make use of the absorption of NF_2 radicals at 2600 \AA (4). In addition, Suprasil quartz (Amersil Quartz

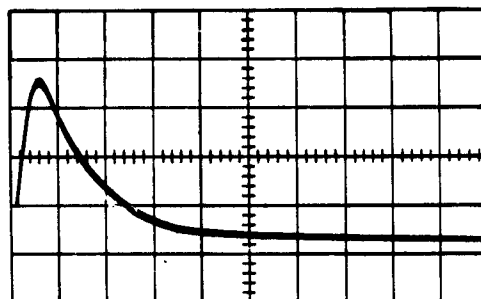


FIGURE 3. PHOTOLYSIS FLASH

20 $\mu\text{sec}/\text{div.}$

Ar PRESSURE, 75 torr

VOLTAGE, 8 kv

CAPACITANCE, 40 μf

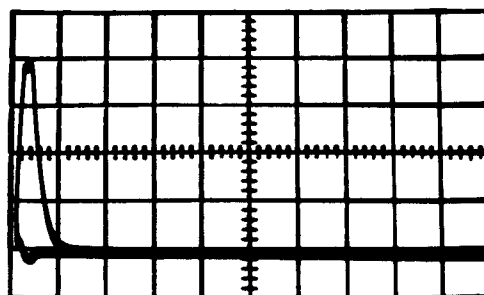


FIGURE 4. SOURCE FLASH

20 $\mu\text{sec}/\text{div.}$

Ar PRESSURE, 75 torr

VOLTAGE, 10 kv

CAPACITANCE, 2 μf

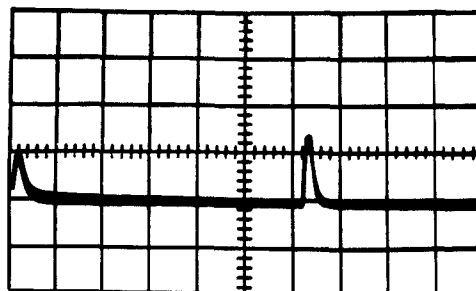


FIGURE 5. MAXIMUM TIME DELAY

50 μ sec/div.

PHOTOLYSIS FLASH, ~ 3 kv AT 10 torr Ar PRESSURE

SOURCE FLASH, 10 kv AT 75 torr Ar PRESSURE



**FIGURE 6. SPECTRAL DISTRIBUTION OF SOURCE FLASH WITH IRON-
ARC CALIBRATION**

Division, Englehardt Industries), which has appreciable transmission at 1700 A, has been ordered. Apparatus with this extended transmission range will permit the use of oxygen as a sensitizer and may permit the direct photolysis of some of the compounds of interest.

FUTURE WORK

Kinetic measurements are expected to be obtained by both thermal and photolytic dissociation experiments during the next quarter. Apparatus is being assembled to permit photolysis experiments to be carried by ultraviolet radiation in the 1700 to 2000 A range. This will make it possible to use oxygen as the sensitizer for some of the compounds, and the possibility of direct photolysis of some compounds of interest will be explored.

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- (3) A. B. Callear, Discussions Faraday Soc., 33, 22 (1962).
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